

# PATENT SPECIFICATION

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## (54) OLEFIN POLYMERIZATION

(71) We, MONTECATINI EDISON S.p.A., A Body Corporate organised and existing under the laws of Italy, of 31 Foro Buonaparte, Milan, Italy, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to catalysts for the polymerization of olefins, that is ethylene or a mixture thereof with another olefin and/or diolefin. Catalysts according to the invention have shown high activity and so make it possible to obtain a large quantity of polymer per unit of catalyst used.

Catalysts according to the invention comprise the product obtained by reaction of a hydride or organometallic compound of a metal of Groups I, II or III of the Periodic System with the product prepared by contacting a titanium compound with a carrier comprising an anhydrous manganese halide, preferably manganous chloride or bromide, in an activated form. The reagents may be brought into contact under conditions in which an activation of the halide occurs or by using the halide itself in a preactivated form so that, either way, the contacting is with the carrier in an activated form.

The activated form of manganous halide preferably has in its X-ray spectrum the refraction of greatest intensity in the spectrum of the inactive halide of lower intensity and/or a surface area greater than 3 sq m/g, preferably greater than 10 sq m/g. Anhydrous manganese chloride gives an active form having in its X-ray spectrum the refraction at  $d=2.57 \text{ \AA}$  (which is the most intense in the spectrum of the inactive halide) of lower intensity and in its place a diffused halo.

Active forms of manganese halides may be obtained by various methods. One of the

most suitable comprises dissolving the anhydrous halide in an alcohol, ester, ether or other anhydrous organic solvent, removing most of the solvent by a fast evaporation, and completing the removal at reduced pressure and in general at above  $100^{\circ}\text{C}$ , preferably from  $150^{\circ}$  to  $400^{\circ}\text{C}$ . Activated forms of the halides may also be obtained by very fine grinding or, in general, by any other mechanical method in which the particles of the carrier are subjected to the action of frictional and/or sliding forces.

The preferred method for the preparation of a supported catalyst component comprises dispersing the titanium compound on the anhydrous manganese halide, already in the active form, by the grinding together mixtures of the two compounds. The grinding is preferably carried out in a ball mill in dry conditions in the absence of any diluents. The preparation may alternatively be carried out by simply mixing the titanium compound with the anhydrous manganese halide in an active form. A suitable method for the preparation of the manganese halide in an active form which at the same time leads to the formation of a supported catalyst component comprises treating the anhydrous manganese halide, not activated, with a normally liquid titanium compound, or with a solution of a titanium compound in an organic solvent, under conditions in which a certain quantity of the titanium compound becomes anchored on the carrier.

It is possible to obtain supported catalytic components directly usable for polymerization by treating anhydrous manganous chloride of the normal type with an excess of titanium tetrachloride at the boiling point and then removing the titanium tetrachloride. This method of preparation of the supported catalyst causes both the activation of the halide and the supporting of the titanium

[Price

compound at one time without having to revert to mechanical activation of the carrier and/or the dispersion of the titanium compound.

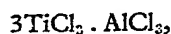
- 5 Titanium compounds which are suitable for use according to the invention include halides, oxyhalides, alcoholates, haloalcoholates, halo-
- 10 titanates, ammonium or alkyl - ammonium titanites, titanites of alkali metals, amides or haloamides, salts of carboxylic acids, and addition compounds of di-, tri- and tetra-
- 15 valent titanium with electron-donor compounds, in which the electron-donor atoms are preferably nitrogen, phosphorus, oxygen or sulphur atoms, for instance: the ethers, phosphines, amines and thioethers. Other
- 20 usable titanium compounds are obtainable from those indicated above and alcoholates and amides of the alkali metals, for instance these of the formula:



and



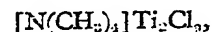
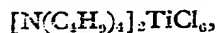
- ( $\text{C}_{12}\text{H}_5\text{N}$  indicates the carbazyl radical).  
25 Typical examples are:



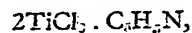
- 30  $\text{Ti}(\text{OC}_2\text{H}_5)_2\text{Cl}_2,$



- 35  $\text{Ti}[\text{N}(\text{C}_6\text{H}_5)_2]_4,$



- 40  $\text{TiBr}_4 \cdot \text{O}(\text{C}_2\text{H}_5)_2,$



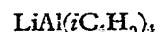
and



- 45 (lithium - titanium tetracarbazyl).

The quantity of titanium compound usable may be within a wide range, generally from below 0.01% to above 30% by weight with respect to the carrier. Particularly interesting results, as far as the yield in polymer per unit of catalyst as to both the titanium compound and the carrier are obtained with quantities of titanium compound of from 1 to 10% by weight with respect to the carrier.

Hydrides and organometallic compounds particularly suited for the preparation of the catalyst are those of the formula:



and



The molar ratio between such compound and the titanium compound is not critical but in the homopolymerization of ethylene may be from 50 to 1000.

Olefin (co)polymerization with such catalysts may be affected in the liquid phase, either in the presence or absence of an inert solvent, or in a gaseous phase. The (co)polymerization temperature may generally be from  $-80^\circ$  to  $200^\circ\text{C}$ , but is preferably from  $50^\circ$  to  $100^\circ\text{C}$  and the pressure either atmospheric or above or below atmospheric. The regulation of the molecular weight of the polymer during the (co)polymerization is carried out with an alkyl halide, organometallic compound of zinc or cadmium, or hydrogen. Such regulation, even to low or very low values, does not cause any appreciable drop of the activity of the catalyst. In the homopolymerization of ethylene it is possible, for instance, to regulate the molecular weight of the polyethylene within a range of practical interest corresponding to values of the intrinsic viscosity, in tetralin at  $135^\circ\text{C}$ , of from 1 to 3 dl/g, without that the yield in polymer dropping to values below which it would become necessary to carry

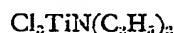
out a purification of the polymer to rid it of catalyst residues.

The polyethylene obtained with the catalysts of the invention is a substantially linear and highly crystalline polymer having density values equal to or greater than 0.96 g/cc, with high processability. The titanium contents in the unpurified polymer is below 10 parts per million.

The invention is illustrated by the following Examples. Where not specifically indicated, the percentages in the Examples are by weight and the intrinsic viscosities measured in tetralin at 135°C.

#### Example 1

30 g of anhydrous manganous chloride ( $\text{MnCl}_2$ ) were dissolved in 100 cc of anhydrous ethanol. By a rapid evaporation of the alcohol and subsequent drying at 300°C under a pressure of 0.5 mm Hg, there was obtained a powder with a specific surface area of 22 sq m/g. 4.7380 g of this powder and 0.1766 g of a compound of the formula



were ground together under a nitrogen atmosphere for 40 hours at 20°C in a glass mill (length 100 mm; diameter 50 mm), containing 550 g of steel balls each having a diameter of 9.5 mm. 0.0130 g of the mixture thus ground and 1500 cc of *n*-heptane were introduced together with 2 cc of aluminium tri-iso-butyl



under a nitrogen atmosphere into a three litre stainless steel autoclave fitted with an anchor-stirrer and heated up to 80°C. Ethylene (10 atm) and hydrogen (5 atm) were added and this pressure was maintained constant throughout the test by continuously introducing ethylene into the autoclave. After 5 hours the polymerization was interrupted and the polymer obtained was filtered and dried. There were obtained 75.5 g of granular polyethylene having an apparent density of 0.39 g/cc and an intrinsic viscosity of 1.91 dl/g. The yield in polymer was 765,000 g/g of titanium.

#### Example 2

6.7423 g of manganese chloride prepared as in Example 1 and 0.1590 g of a compound of the formula



were ground together for 20 hours under a nitrogen atmosphere at 20°C. 0.0280 g of the mixture thus prepared were used for the polymerization of the ethylene as in Example 1. There were obtained 88 g of a polyethylene having an intrinsic viscosity of 2.27 dl/g.

The yield in polymer was 610,000 g/g of titanium.

#### Example 3

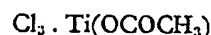
13.1640 g of manganous chloride prepared as in Example 1 and 0.5690 g of a compound of the formula



were ground together under a nitrogen atmosphere for 16 hours at 20°C. 0.0268 g of the mixture thus prepared were used for the polymerization of the ethylene as in Example 1. There were obtained 149 g of granular polyethylene having an intrinsic viscosity of 2.2 dl/g. The yield in polymer was 772,000 g/g of titanium.

#### Example 4

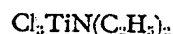
7.5410 g of manganous chloride prepared as in Example 1 and 0.2380 g of a compound of the formula



were ground together under a nitrogen atmosphere for 3 hours at 20°C. 0.021 g of the mixture thus obtained were used for the polymerisation of the ethylene as in Example 1. There were obtained 22.5 g of polyethylene having an intrinsic viscosity of 3.6 dl/g. The yield in polymer was 156,000 g/g of titanium.

#### Example 5

A solution, prepared by dissolving 25 g of anhydrous manganous bromide ( $\text{MnBr}_2$ ) in 100 cc of anhydrous ethanol, was slowly dropped into a cylindrical vessel heated to 150°C under subatmospheric pressure. The powder thus obtained was dried by heating at 300°C and 0.5 mm Hg. 12.3460 g of manganous bromide thus treated and 0.4320 g of a compound of the formula



were ground together for 3 hours under a nitrogen atmosphere at 20°C. 0.0210 g of this mixture was used in the polymerization of ethylene as in Example 1. There were obtained 53.5 g of a polyethylene with an intrinsic viscosity of 2.25 dl/g. The yield in polymer was 357,000 g/g of titanium.

#### Example 6

Into a 1000 cc three-necked glass flask fitted with a stirrer and a reflux coolant there were introduced under an anhydrous nitrogen atmosphere 25 g of manganous chloride and 700 cc of anhydrous tetrahydrofuran. The resulting suspension was maintained at the boiling point for 40 hours. After cooling the supernatant liquid was removed by decantation and the insoluble product remaining was

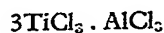
dried at 0.5 mm Hg and 260°C. 15.7779 g of the manganous chloride so obtained and 0.5468 g of a compound of the formula



- 5 were ground together under a nitrogen atmosphere for 16 hours at 20°C. 0.021 g of the mixture thus prepared was used for the polymerization of the ethylene as described in Example 1. There were obtained 68 g of a polyethylene having an intrinsic viscosity of 2.35 dl/g. The yield in polymer was 555,000 g/g of titanium.

#### Example 7

- 15 10.230 g of manganous chloride prepared as in Example 1 and 0.97 g of a compound of the formula



- 20 were ground together under a nitrogen atmosphere for 16 hours at 20°C. 0.051 g of the mixture was used for the polymerization of the ethylene as in Example 1. There were obtained 530 g of a polyethylene which had an intrinsic viscosity of 2.38 dl/g. The yield in polymer was 490,000 g/g of titanium.

#### Example 8

- 25 4.4530 g of manganous chloride prepared as in Example 1 and 0.7230 g of a compound of the formula



- 30 were ground together under a nitrogen atmosphere for 16 hours at 20°C. 0.0140 g of the mixture thus prepared and aluminium di-iso-butyl hydride



- 35 were used in the polymerization of ethylene as in Example 1. There were obtained 146 g of a polyethylene which had an intrinsic viscosity of 2.72 dl/g. The yield in polymer was 350,000 g/g of titanium.

#### Example 9

- 40 Example 8 was repeated except that aluminium triethyl

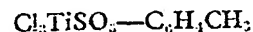


- 45 instead of the iso-butyl hydride. 0.0110 g of the mixture were used as in Example 8. There were obtained 49 g of a polyethylene which had an intrinsic viscosity of 1.97 dl/g. The yield in polymer was 150,000 g/g of titanium.

#### Example 10

- 50 6.2020 g of manganous chloride prepared

as in Example 1 and 0.4400 g of a compound of the formula



were ground together under a nitrogen atmosphere for 16 hours at 20°C. 0.020 g of the mixture thus prepared were used in the polymerization of the ethylene as in Example 1. There were obtained 103 g of a polyethylene which had an intrinsic viscosity of 2.32 dl/g. The yield in polymer was 530,000 g/g of titanium.

#### Example 11

5.7470 g of manganous chloride prepared as in Example 1 and 0.3070 g of a compound of the formula



(obtained by reacting equimolar quantities of titanium trichloride with titanium tetraisopropylate in xylene at 120°C) and showing an analysis:

Found Ti=25.23% Calculated Ti=25.25%;  
Found Cl=27.90% Found Cl=28.95%

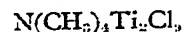
were ground together under a nitrogen atmosphere for 16 hours at 20°C. 0.020 g of the mixture thus prepared were used for the polymerization of the ethylene as in Example 1. There were obtained 54 g of a polymer having an intrinsic viscosity of 2.35 dl/g. The yield in polymer was 210,000 g/g of titanium.

#### Example 12

Into the mill used in Example 1 there were ground for 16 hours at 20°C 0.300 g of titanium tetrachloride and 4.4757 g of manganous chloride prepared as in Example 1. 0.0140 g of the mixture so prepared was used in the polymerization of ethylene as in Example 1. There were obtained 222 g of a polyethylene which had an intrinsic viscosity of 2.03 dl/g. The yield in polymer was 1,000,000 g/g of titanium.

#### Example 13

8.58 g of manganous chloride prepared as in Example 1 and 0.56 g of a compound of the formula



were ground together for 3 hours at 20°C in the mill used in Example 1. 0.0736 g of the mixture thus ground were introduced together with 1000 cc of n-heptane and 2 cc of aluminium tri-isobutyl



under a nitrogen atmosphere into a 2 litre

- 5 stainless autoclave fitted with an anchor stirrer and heated up to 85°C. To this mass there was added ethylene (10 atm) and hydrogen (5 atm). The pressure was maintained constant by continuously introducing ethylene.
- 10 After 8 hours the polymerization was interrupted, the reaction product was filtered off and the polymer obtained was dried. There were obtained 187 g of a polyethylene which had an intrinsic viscosity of 2.17 dl/g. The yield in polymer was 213,000 g/g of titanium.

#### Example 14

- 15 6.48 g of manganous chloride prepared as in Example 1 and 0.71 g of a compound of the formula



- 20 were ground together for 16 hours at 20°C in the mill used in Example 1. 0.036 g of the mixture thus prepared was used in the polymerization of ethylene as in Example 13. There were obtained 137 g of polyethylene having an intrinsic viscosity of 2.68 dl/g. The yield in polymer was 410,000 g/g of titanium.

#### Example 15

- 25 9.9 g of manganous chloride dried at 300°C under a pressure of 0.5 mm Hg were treated with 100 cc of boiling titanium tetrachloride (at about 140°C) for 2.5 hours. This mass was hot filtered, and the solid was washed with *n*-heptane until all chloride ions in the filtrate disappeared and finally dried under vacuum. In the isolated solid there was 0.08% of titanium. 1.160 g of this product
- 30 was used in the polymerization of the ethylene as in Example 1. There were obtained 112 g of a polyethylene having an intrinsic viscosity of 2.70 dl/g. The yield in polymer was 120,000 g/g of titanium.

- 40 WHAT WE CLAIM IS:—

1. A catalyst for the polymerization of olefins comprising a product obtained by reaction of a hydride or organometallic compound of a metal of Groups I, II or III of the Periodic System with a product prepared by contacting a titanium compound with a carrier comprising an anhydrous manganese halide in an active form.

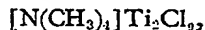
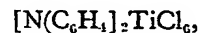
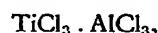
2. A catalyst according to claim 1 in which the manganese halide is manganous chloride or bromide.

3. A catalyst according to claim 1 or claim 2 in which the titanium compound is a halide, oxyhalide, alcoholate, haloalcoholate, halo-titanate, ammonium or alkyl - ammonium - alkyl titanate, titanite of an alkali metal, amide, haloamide, salt of a carboxylic acid, or addition compound of di-, tri- or tetra-valent titanium with an electron-donor compound.

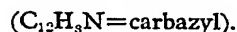
4. A catalyst according to any of the preceding claims in which the active manganese halide has in its X-ray spectrum the refraction of greatest intensity in the spectrum of the inactive halide of lower intensity and/or a surface area greater than 3 sq m/g.

5. A catalyst according to claim 4 in which the active manganese halide has a surface area greater than 10 sq m/g.

6. A catalyst according to any of the preceding claims in which the titanium compound has the formula:



or



7. A catalyst according to any of the preceding claims in which the titanium compound is present on the carrier to the extent of from 1% to 10% by weight with respect to the carrier.

8. A catalyst according to any of the preceding claims in which as hydride or organometallic compound, an aluminium hydride or alkyl compound is used.

9. A catalyst according to claim 8 in which an aluminium trialkyl is used.

10. A method of preparing a catalyst

- according to any of the preceding claims in which a titanium compound is contacted with an anhydrous manganese halide in an active form obtained by dissolving an anhydrous manganese halide in an organic solvent rapidly evaporating most of the solvent and completing the removal under reduced pressure and at above 100°C.
- 5 11. A method according to claim 10 in which the organic solvent is an alcohol, ester or ether.
- 10 12. A method of preparing a catalyst according to any of claims 1 to 9 in which a titanium compound is contacted with an activated anhydrous manganese halide by grinding together the two compounds.
- 15 13. A method according to claim 12 in which the grinding is effected in a ball mill in the absence of a solvent.
- 20 14. A method of preparing a catalyst according to any of claims 1 to 9 in which the supported catalyst component is obtained by treating an inactive anhydrous manganese halide with a liquid titanium compound or with a solution of a titanium compound in an organic solvent under conditions in which the titanium compound becomes anchored onto the carrier.
15. A method of preparing a catalyst according to any of claims 1 to 9 in which an anhydrous manganese halide is contacted with an excess of titanium tetrachloride at the boiling point and removing the excess.
- 30 16. A catalyst prepared by a method according to any of claims 10 to 15.
- 35 17. A catalyst for the polymerization of olefins as described in any of the Examples.
18. A process for the polymerization of ethylene or of a mixture thereof with another alpha - olefin and/or diolefin which is carried out in the presence of a catalyst according to any of claims 1 to 9 or 17.
- 40 19. A process for the polymerization of olefins as described in any of the Examples.
20. An olefin polymer prepared according to the process of claims 18 or 19.
- 45

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